

Ch 27 Gravimetric Analysis

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Analytical chemistry

Classification by the techniques:

1. Classical Analysis

Gravimetric, Titration(Volumetric) Analysis

2. Instrumental Analysis

Electrochemical Analysis,

Spectrochemical Analysis,

Chromatographic Separation and Analysis

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Ch 12 Gravimetric Analysis

gravi – metric
(weighing - measure)

Definition: A precipitation or volatilization method based on the determination of weight of a substance of known composition that is chemically related to the **analyte**.

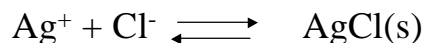
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12.1 Procedure

Criteria

(1) The desired substance: completely precipitated.

"common ion" effect can be utilized:



excess of Cl^- which is added

(2) The weighed form: known composition.

(3) The product: "pure", easily filtered..

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12. 1 Procedure

- 7 Steps in Gravimetric Analysis

- 1) Dry and weigh sample
- 2) Dissolve sample
- 3) Add **precipitating reagent** in excess
- 4) **Coagulate** precipitate usually by heating
- 5) Filtration-separate precipitate from **mother liquor**
- 6) Wash precipitate
- 7) Dry and weigh to **constant weight** (0.2-0.3 mg)

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Suction Filtration

- Filter flask
- Buchner funnel
- Filter paper
- Glass frit
- Filter adapter
- Heavy-walled rubber tubing
- Water aspirator



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Suction Filtration

- Mother liquor



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12.2

Advantages/Disadvantages

- Experimentally simple and elegant
- Accurate
- Precise (0.1-0.3 %)
- Macroscopic technique-requires at least 10 mg ppt to collect and weigh properly
- Time-consuming (1/2 day?)

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12.3 Calculation

- Design of experiment
- Content Calculation
- Evaluation of the results

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12.3 Calculation

- % of analyte, % A
- $\%A = \frac{\text{weight of analyte}}{\text{weight of sample}} \times 100$
- weight of ppt directly obtained $\rightarrow \%A$

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How Do We Get %A?

- % A = $\frac{\text{weight of ppt} \times \text{gravimetric factor (G.F.)}}{\text{weight of sample}} \times 100$
- G.F. = $\frac{a \text{ FW[analyte]}}{b \text{ FW[precipitate]}}$
- G.F. = # gms of analyte per 1 gm ppt

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The Gravimetric Factor

- G.F. = $\frac{a \text{ FW[analyte]}}{b \text{ FW[precipitate]}}$
- | <u>Analyte</u> | <u>ppt</u> | <u>G.F.</u> |
|--|----------------------------------|-------------|
| CaO | CaCO ₃ | |
| FeS | BaSO ₄ | |
| UO ₂ (NO ₃) ₂ ·6H ₂ O | U ₃ O ₈ | |
| Cr ₂ O ₃ | Ag ₂ CrO ₄ | |

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Gravimetric Factor

<u>Analyte</u>	<u>ppt</u>	<u>G.F.</u>
CaO	CaCO ₃	CaO/CaCO ₃
FeS	BaSO ₄	FeS/BaSO ₄
UO ₂ (NO ₃) ₂	U ₃ O ₈	3UO ₂ (NO ₃) ₂ /U ₃ O ₈
Cr ₂ O ₃	Ag ₂ CrO ₄	Cr ₂ O ₃ /2Ag ₂ CrO ₄

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Problem

- Consider a 1.0000 g sample containing 75% potassium sulfate (FW 174.25) and 25% MSO₄. The sample is dissolved and the sulfate is precipitated as BaSO₄ (FW 233.39). If the BaSO₄ ppt weighs 1.4900, what is the atomic weight of M²⁺ in MSO₄?
- ANS: Mg²⁺

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Answer

- The hard part is setting up the correct equation

$$1.4900 = \frac{0.75 * 233.39}{174.25} + \frac{0.25 * 233.39}{x + 96.06}$$

- Rearranging and solving:

$$0.4855 = \frac{58.3475}{x + 96.06}; x = 24.12(\text{Mg}^{2+})$$

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Problem

- A mixture of mercurous chloride (FW 472.09) and mercurous bromide (FW 560.99) weighs 2.00 g. The mixture is quantitatively reduced to mercury metal (At wt 200.59) which weighs 1.50 g. Calculate the % mercurous chloride and mercurous bromide in the original mixture.
- ANS: 0.5182 g

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Answer

- Again, important to set up correct equation:

$$1.50 = \frac{2 * 200.59 * x}{472.09} + \frac{2 * 200.59(2 - x)}{560.99}$$

- Rearranging and solving:

$$0.8498 + 0.7151(2 - x) = 1.50$$

$$x = 0.5182g$$

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- Example: How many mL of 1% potassium chloride would be needed to precipitate all of the silver in a 0.5 g ore sample that contains 1.5 parts per thousand silver? Allow for a 50% excess of the chloride solution.

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12.4 Representative Gravimetric Analyses

Table 27-1 Representative gravimetric analyses

Species analyzed	Precipitated form	Form weighed	Interfering species
K ⁺	KB(C ₆ H ₅) ₄	KB(C ₆ H ₅) ₄	NH ₄ ⁺ , Ag ⁺ , Hg ²⁺ , TI ⁺ , Rb ⁺ , Cs ⁺
Mg ²⁺	Mg(NH ₄)PO ₄ ·6H ₂ O	Mg ₂ P ₂ O ₇	Many metals except Na ⁺ and K ⁺
Ca ²⁺	CaC ₂ O ₄ ·H ₂ O	CaCO ₃ or CaO	Many metals except Mg ²⁺ , Na ⁺ , K ⁺
Ba ²⁺	BaSO ₄	BaSO ₄	Na ⁺ , K ⁺ , Li ⁺ , Ca ²⁺ , Al ³⁺ , Cr ³⁺ , Fe ³⁺ , Sr ²⁺ , Pb ²⁺ , NO ₃ ⁻
Ti ⁴⁺	TiO(5,7-dibromo-8-hydroxyquinoline) ₂	Same	Fe ³⁺ , Zr ⁴⁺ , Cu ²⁺ , C ₂ O ₄ ²⁻ , citrate, HF
VO ₄ ³⁻	Hg ₂ VO ₄	V ₂ O ₅	Cl ⁻ , Br ⁻ , I ⁻ , SO ₄ ²⁻ , CrO ₄ ²⁻ , AsO ₄ ³⁻ , PO ₄ ³⁻
Cr ³⁺	PbCrO ₄	PbCrO ₄	Ag ⁺ , NH ₄ ⁺
Mn ²⁺	Mn(NH ₄)PO ₄ ·H ₂ O	Mn ₂ P ₂ O ₇	Many metals
Fe ³⁺	Fe(HCO ₂) ₃	Fe ₂ O ₃	Many metals
Co ²⁺	Co(1-nitroso-2-naphtholate) ₄	CoSO ₄ (by reaction with H ₂ SO ₄)	Fe ³⁺ , Pd ²⁺ , Zr ⁴⁺

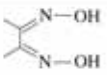
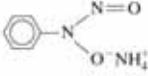

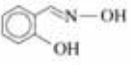
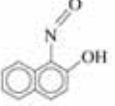
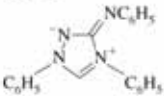
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Table 27-1 Representative gravimetric analyses

Species analyzed	Precipitated form	Form weighed	Interfering species
Ni ²⁺	Ni(dimethylglyoximate) ₂	Same	Pd ²⁺ , Pt ²⁺ , Bi ³⁺ , Au ³⁺
Cu ²⁺	CuSCN	CuSCN	NH ₄ ⁺ , Pb ²⁺ , Hg ²⁺ , Ag ⁺
Zn ²⁺	Zn(NH ₄)PO ₄ ·H ₂ O	Zn ₂ P ₂ O ₇	Many metals
Ce ⁴⁺	Ce(IO ₃) ₄	CeO ₂	Th ⁴⁺ , Ti ⁴⁺ , Zr ⁴⁺
Al ³⁺	Al(8-hydroxyquinolate) ₃	Same	Many metals
Sn ⁴⁺	Sn(cupferron) ₄	SnO ₂	Cu ²⁺ , Pb ²⁺ , As(III)
Pb ²⁺	PbSO ₄	PbSO ₄	Ca ²⁺ , Sr ²⁺ , Ba ²⁺ , Hg ²⁺ , Ag ⁺ , HCl, HNO ₃
NH ₄ ⁺	NH ₄ B(C ₆ H ₅) ₄	NH ₄ B(C ₆ H ₅) ₄	K ⁺ , Rb ⁺ , Cs ⁺
Cl ⁻	AgCl	AgCl	Br ⁻ , I ⁻ , SCN ⁻ , S ²⁻ , S ₂ O ₃ ²⁻ , CN ⁻
Br ⁻	AgBr	AgBr	Cl ⁻ , I ⁻ , SCN ⁻ , S ²⁻ , S ₂ O ₃ ²⁻ , CN ⁻
I ⁻	AgI	AgI	Cl ⁻ , Br ⁻ , SCN ⁻ , S ²⁻ , S ₂ O ₃ ²⁻ , CN ⁻
SCN ⁻	CuSCN	CuSCN	NH ₄ ⁺ , Pb ²⁺ , Hg ²⁺ , Ag ⁺
CN ⁻	AgCN	AgCN	Cl ⁻ , Br ⁻ , I ⁻ , SCN ⁻ , S ²⁻ , S ₂ O ₃ ²⁻
F ⁻	(C ₆ H ₅) ₃ SnF	(C ₆ H ₅) ₃ SnF	Many metals (except alkali metals), SiO ₄ ⁴⁻ , CO ₃ ²⁻
ClO ₄ ⁻	KClO ₄	KClO ₄	
SO ₄ ²⁻	BaSO ₄	BaSO ₄	Na ⁺ , K ⁺ , Li ⁺ , Ca ²⁺ , Al ³⁺ , Cr ³⁺ , Fe ³⁺ , Sr ²⁺ , Pb ²⁺ , NO ₃ ⁻
PO ₄ ³⁻	Mg(NH ₄)PO ₄ ·6H ₂ O	Mg ₂ P ₂ O ₇	Many metals except Na ⁺ , K ⁺
NO ₃ ⁻	Nitron nitrate	Nitron nitrate	ClO ₂ ⁻ , I ⁻ , SCN ⁻ , CrO ₄ ²⁻ , ClO ₃ ⁻ , NO ₂ ⁻ , Br ⁻ , C ₂ O ₄ ²⁻
CO ₃ ²⁻	CO ₂ (by acidification)	CO ₂	(The liberated CO ₂ is trapped with Ascarite and weighed.)

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Table 27-2 Common organic precipitating agents

Name	Structure	Ions precipitated
Dimethylglyoxime		Ni ²⁺ , Pd ²⁺ , Pt ²⁺
Cupferron		Fe ³⁺ , VO ₂ ⁺ , Ti ⁴⁺ , Zr ⁴⁺ , Ce ⁴⁺ , Ga ³⁺ , Sn ⁴⁺
8-Hydroxyquinoline (oxine)		Mg ²⁺ , Zn ²⁺ , Cu ²⁺ , Cd ²⁺ , Pb ²⁺ , Al ³⁺ , Fe ³⁺ , Bi ³⁺ , Ga ³⁺ , Th ⁴⁺ , Zr ⁴⁺ , UO ₂ ²⁺ , TiO ₂ ²⁺
Salicylaldehyde		Cu ²⁺ , Pb ²⁺ , Bi ³⁺ , Zn ²⁺ , Ni ²⁺ , Pd ²⁺
1-Nitroso-2-naphthol		Co ²⁺ , Fe ³⁺ , Pd ²⁺ , Zr ⁴⁺
Nitron		NO ₂ ⁻ , ClO ₂ ⁻ , BF ₄ ⁻ , WO ₄ ²⁻
Sodium tetrphenylborate Tetraphenylarsonium chloride	Na ⁺ B(C ₆ H ₅) ₄ ⁻ (C ₆ H ₅) ₄ As ⁺ Cl ⁻	K ⁺ , Rb ⁺ , Cs ⁺ , NH ₄ ⁺ , Ag ⁺ , organic ammonium ions Cr ₂ O ₇ ²⁻ , MnO ₄ ⁻ , ReO ₄ ⁻ , MoO ₄ ²⁻ , WO ₄ ²⁻ , ClO ₄ ⁻ , I ₃ ⁻

12.5 The Precipitation Process

1. Particle Size / Filterability

- produce particles large enough to be 'caught'
- ideally, produce crystals
- avoid colloidal suspension

Partide size and filterability

Colloidal Suspensions

Size range: 10^{-6} - 10^{-4} mm

No tendency to settle

Difficult or impossible to filter

Crystalline suspensions

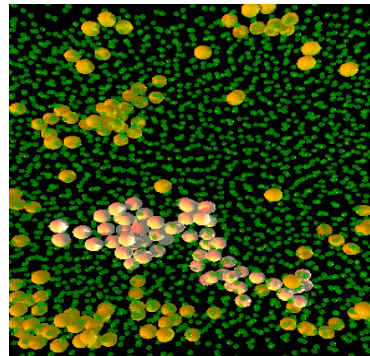
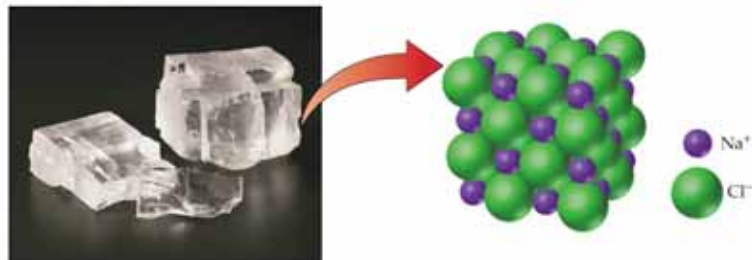
Size Range: 10^1 - 10 mm

Will settle spontaneously

Readily filtered

Typically of higher purity than colloids

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2. Mechanism of Precipitation

Crystal Forming:

nucleation

particle growth

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Mechanisms of precipitation

Two competing processes

Nucleation

When a small number of ions, atoms, molecules initially unite.

Spontaneous

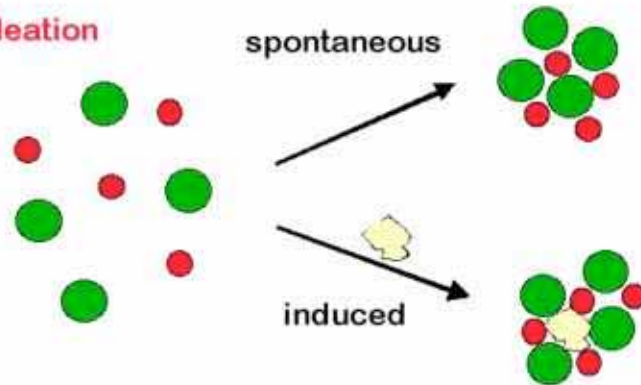
Induced

Particle growth

The three dimensional growth of a particle nucleus into a larger crystal.

Mechanisms of precipitation

Nucleation



Spontaneous nucleation will occur on its own.

Induced nucleation requires a 'seed' particle to get things started (dust, another crystal, glass fragment, ...)

Mechanisms of precipitation

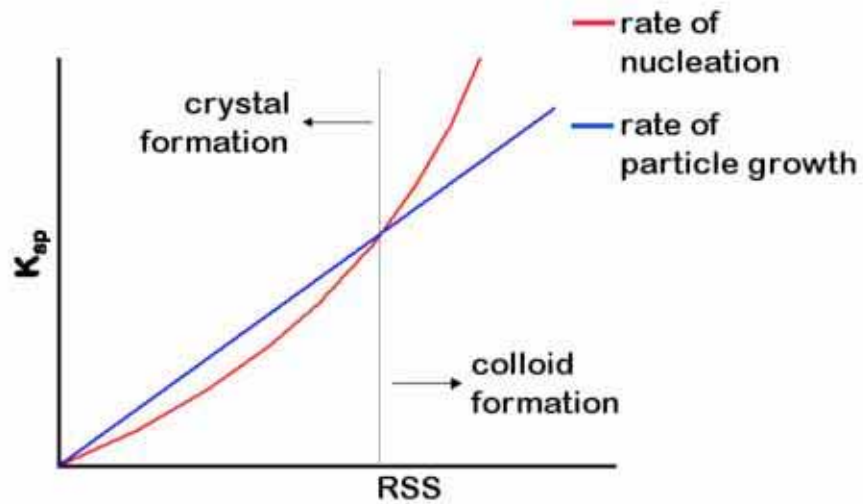
Particle growth



Once a nucleation site has formed, other ions are attracted to the site. This will result in the formation of large, filterable particles.

If done properly, it also reduces contaminants since they don't 'fit in' to the crystal structure.

Mechanisms of precipitation



Particle size and filterability

We have some control on particle size based on how we add our reagents.

Relative supersaturation (RSS)

$$RSS = \frac{Q - S}{Q}$$

Where

Q = concentration of solute at any time

S = equilibrium solubility of solute

RSS can be used estimate/control the type of precipitate that is formed.

Mechanisms of precipitation

Rate of nucleation is $\propto e^{-Q/RT} \propto RSS$

Rate of particle formation is $\propto RSS$

If **RSS is large**, nucleation is favored and colloidal suspensions tend to be formed.

If **RSS is small**, particle growth will predominate resulting in crystalline precipitates.

Mechanisms of precipitation

The goal is to form crystalline precipitates so RSS must be minimized.

This can be done by:

Increasing S

Elevate temperature, pH control

Decrease Q

Use dilute solutions

Slowly add reagents

Stirring the solution

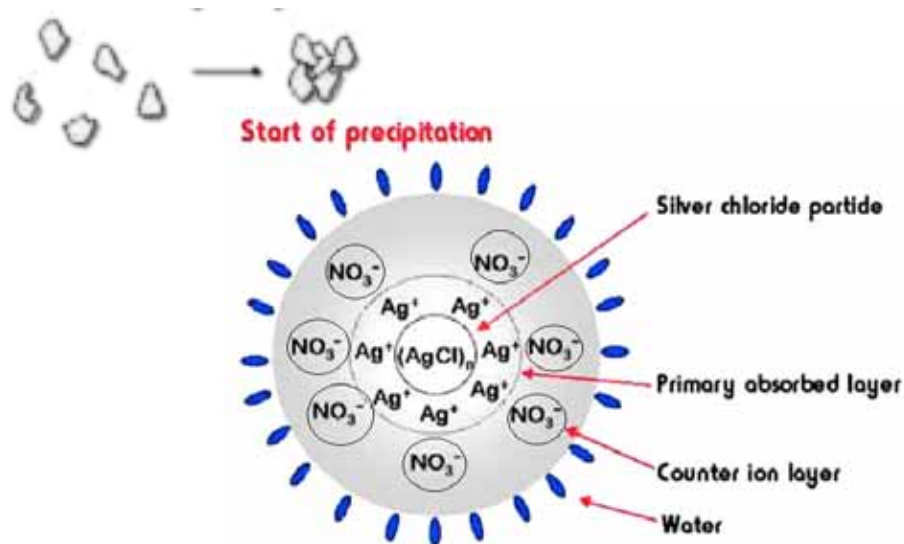
Techniques to promote crystal growth

- (1). **Raising the temperature** to increase S and thereby decrease relative supersaturation.
- (2). **Adding precipitant slowly with vigorous mixing**, to avoid a local, highly supersaturated condition where the stream of precipitant first enters the analyte.
- (3). **Keeping the volume of solution large** so that the concentration of analyte and precipitant are low.

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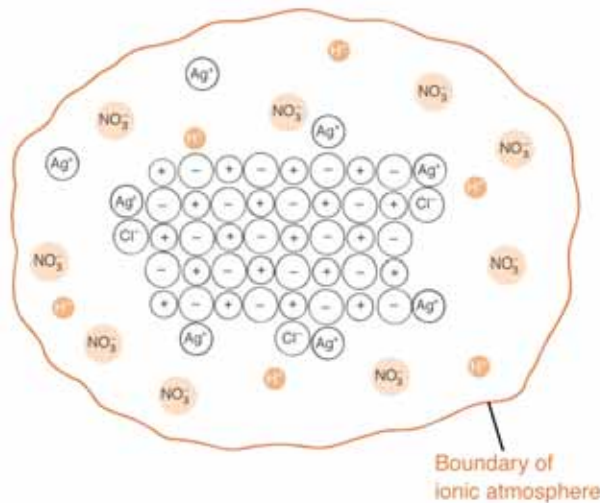
3. Other ways to obtain a good precipitate

(1) Increasing the electrolyte concentration



High Electrolyte Concentration to Aid Precipitation

- (1) Decreasing the volume of the counter-ion layer
- (2) Increasing the chance for coagulation



3. Other ways to obtain a good precipitate

- (2) Using a volatile electrolyte

AgCl , wash with HCl . Drying precipitate at 110°C will remove HCl .

This displaces the less volatile, excess counter ion.

Treatment of colloidal preprecipitates

(3) Digestion and aging

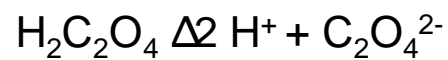
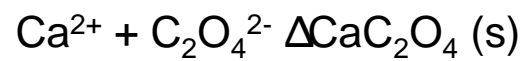
Digestion. Heating the solution for about an hour after precipitate formation. This helps to remove weakly bound water.

Aging. Storing the solution, unheated, overnight. This allows trapped contaminants time to 'work their way out.'

Both can result in a denser precipitate that is easier to filter.

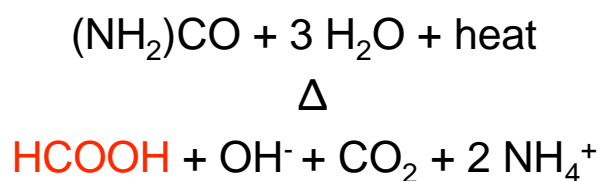
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(4) pH control of precipitation



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(5) Homogeneous Precipitation



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Exercises

1. To obtain a precipitate which is useful for gravimetric analysis, the analyst tries to obtain conditions to encourage crystal growth, as opposed to the formation of a colloid. Which of the following statements aids in the formation of a crystalline precipitate?

- (a) The solution is kept cool to slow down the movement of ions to allow crystals to form.
- (b) The solutions are made as dilute as practical to allow crystals to form slowly.
- (c) The solutions are mixed rapidly to allow the appropriate ions to make contact without interference of other materials.

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Exercises

2. Which of the following processes is true regarding the digestion of a solution containing a precipitate?

- (a) Digestion tends to increase particle size of the precipitate.
- (b) Digestion is used to slow down the coagulation of a colloidal precipitate because of the increased energy added to the solution.
- (c) A long digestion is not recommended because the higher temperatures enable impurities to become trapped in the crystal lattice of the precipitate

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Exercises

3. In the gravimetric analysis of iron, hydroxide may be added to a solution containing Fe^{3+} to precipitate a gelatinous mess which is ignited to form Fe_2O_3 . If 0.2864 grams of Fe_2O_3 were formed from the ignition of the precipitated mess, how many grams of FeCO_3 were contained in the original sample analyzed?

- (a) 0.4155 g FeCO_3
- (b) The answer cannot be computed because the sample did not contain any Fe^{2+} .
- (c) 0.2078 g FeCO_3

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Exercises

4 A sample of ore containing manganese weighed 1.2354 grams. This sample was heated in a solution of nitric acid, which dissolved the manganese ion producing manganese(III) nitrate ($\text{Mn}(\text{NO}_3)_3$). The acidity of the solution was adjusted, and Hydrogen sulfide gas was bubbled into the solution producing 0.2876 grams of manganese(III) sulfide (Mn_2S_3). What is the percentage of manganese in the original sample?

- (a) 12.37% Mn
- (b) 6.19% Mn
- (c) 3.09% Mn

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Exercises

5 Why do you reheat/recool the solid unknown until its weight stabilizes?

- a. To increase the precision of your measurement.
- b. To increase the accuracy of your measurement.
- c. To ensure that there is no water in your solid.
- d. To convert any nickel metal to nickel oxide.

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Exercises

6 In Gravimetric Determination of Nickel, heating gently during the coagulation stage would aid what process?

- a. Precipitation -- more Nickel diglyme would come out of solution.
- b. Digestion -- particle size and purity increases due to recrystallization.
- c. Evaporation -- the solution becomes more concentrated so more precipitation occurs and filtering is easier.
- d. Calculation -- the waiting gives you time to work example problems and ask questions.

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Exercises

7. A certain barium halide exists as the hydrated salt $\text{BaX}_2 \cdot 2\text{H}_2\text{O}$, where X is the halogen. The barium content of the salt can be determined by gravimetric methods. A sample of the halide (0.2650 g) was dissolved in water (200 cm³) and excess sulfuric acid added. The mixture was then heated and held at boiling for 45 minutes. The precipitate (barium sulfate) was filtered off, washed and dried. Mass of precipitate obtained = 0.2533 g. Determine the identity of X.

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Exercises

8. Summarize the conditions to improve an analytical precipitation in Gravimetric analysis.